(12) UK Patent Application (19) GB (11) 2 243 162 (13) A

(43) Date of A publication 23.10.1991

(21) Application No 9107539.0

(22) Date of filing 10.04.1991

(30) Priority data
(31) 02099275 (32) 17.04.1990 (33) JP

(71) Applicant
Kabushiki Kaisha Riken

(Incorporated in Japan)

13-5, Kudan-kita 1-chome, Chiyoda-ku, Tokyo, Japan

(72) Inventors
Katsumi Takiguchi
Masaki Oya
Toru Onuki

(74) Agent and/or Address for Service
Sergeants
25 The Crescent, King Street, Leicester, LE1 6RX, United Kingdom

(51) INT CL[5]
C23C 14/06 14/32

(52) UK CL (Edition K)
C7F FCXX FP820 FR916 F102 F1021 F104 F109 F242 F304 F310
U1S S1783

(56) Documents cited
GB 2178064 A GB 2158104 A US 4226082 A

(58) Field of search
UK CL (Edition K) C7F FCSE FCSL FCSM FCSX FCVE FCVL FCVM FCVX FCXE FCXL FCXM FCXX FPCD FPCE FPCH FPCL FPCP FPCR FPCT FPCX FPDD FPDE FPDH FPDL FPDP FPDR FPDT FPDX FPEE FPEL FPEM FPEX
INT CL[5] C23C
Online databases: WPI, CLAIMS

(54) A chromium nitride coating having a steadily increasing nitrogen concentration

(57) A wear-resistant coating is provided on a base material which includes a nitride of chromium, the nitrogen concentration of the coating being increased from an interface between the base material and the coating continuously towards an outer surface of the coating. The coating is produced by the steps of positioning the base material 1 in a vapor deposition chamber 9; producing chromium vapor in the chamber so that the chromium is deposited to form a coating on the sliding surface of the base material 1, introducing nitrogen into the chamber while the chromium is being deposited so that a nitride of chromium is produced and deposited on the sliding surface of the base material forming at least a part of the coating, the nitrogen concentration in the chamber being continuously increased so that the nitrogen concentration in the coating continuously increases from the interface between the base material and the coating towards the outer surface of the coating. The coating has a layer adjacent to the base material consisting substantially of chromium, whilst the coating may have a layer adjacent to the outer surface consisting substantially of at least one of CrN, Cr_2N and a mixture of Cr_2N and CrN. The coating may be used as the sliding surface of a piston ring of an internal combustion engine.

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F I G. 1

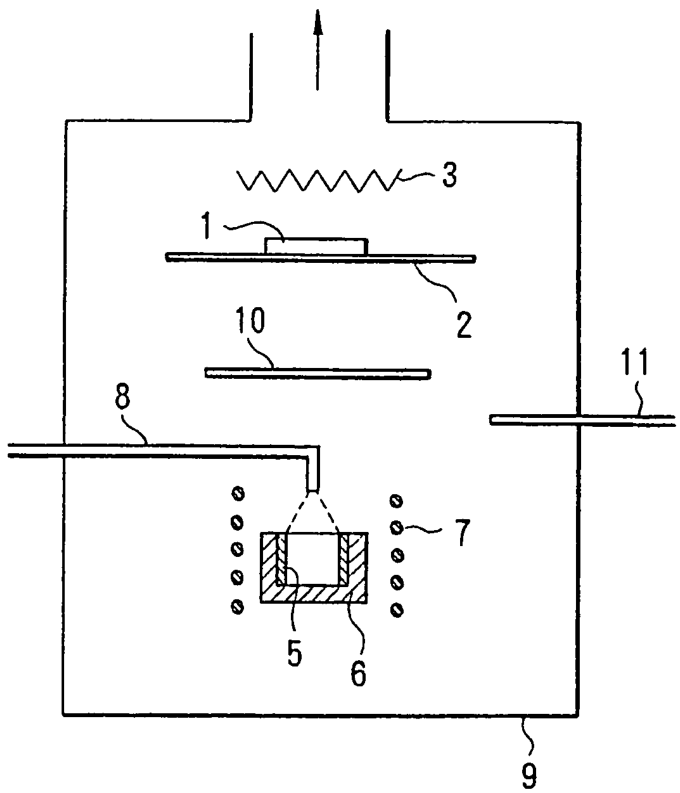


FIG.2

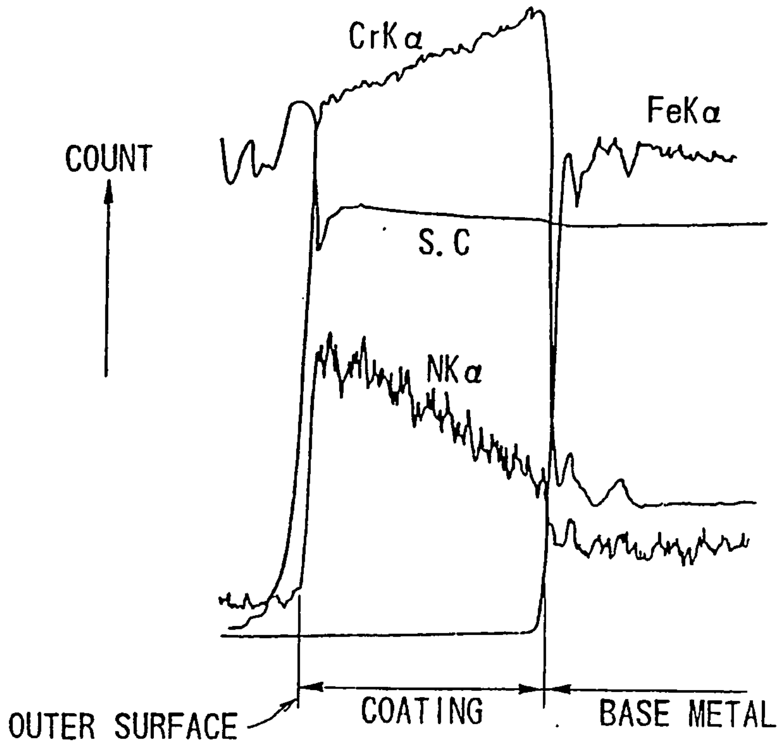
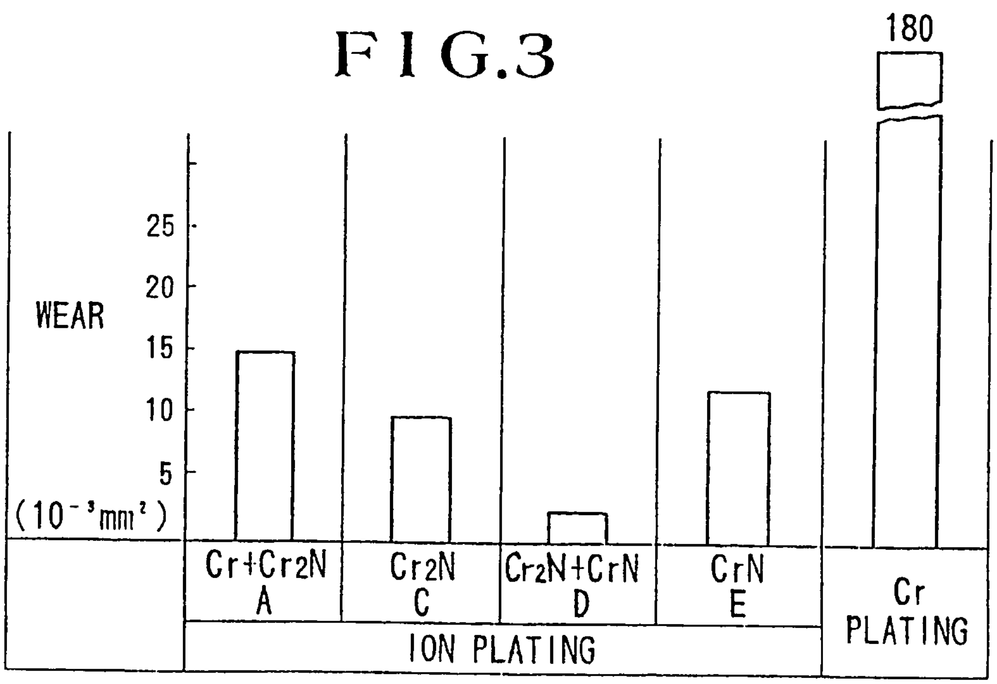

CrKα
FeKα
COUNT
S.C
NKα
OUTER SURFACE
COATING
BASE METAL

FIG.3


180
WEAR
25
20
15
10
5
(10⁻³mm²)
Cr+Cr2N
A
Cr2N
C
Cr2N+CrN
D
CrN
E
ION PLATING
Cr
PLATING

A wear-resistant coating

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a wear-resistant coating on a sliding surface of a structural member and a method of producing the same. More specifically, the present invention pertains to a wear-resistant coating having a high resistance to peeling off from a base material and a method of producing the same. Although not limited to such an application, the coating of the present invention is particularly suitable for use as a wear-resistant coating of a piston ring for an internal combustion engine or the like.

Description of the Prior Art

A piston ring for an internal combustion engine has a sliding surface which is brought into a slidable engagement with a cylinder surface. Thus, the sliding surface of the piston ring is required to possess a high wear-resistant property. To meet this requirement, the sliding surface of the piston ring has conventionally been applied with a hard chromium plating which possesses an excellent wear-resistant property.

It should however be noted that the piston rings for recent internal combustion engines are subjected to a thermal load which is significantly higher than used to be. This is particularly true in the case of engines of very high output power and/or engines provided with measures for decreasing pollutant emisions in exhaust gas. In these piston rings which are subjected to a higher thermal load, it has been

experienced that the conventional hard chromium plating does not provide a sufficient wear resistance. It has therefore been desired to provide a coating for a piston ring which can be used even under an extremely high thermal load.

In order to provide a piston ring which can meet the aforementioned desire, proposals have been made to provide the piston ring with a coating of metal nitrides or metal carbides formed on the sliding surface by means of an ion plating. Examples of such coatings are shown in the Japanese patent disclosure No. 57-57868 and 57-65837. In the patent disclosure No. 57-57868, the piston ring is formed at the sliding surface with a coating of very hard material such as TiN, TiC or CrN by for example a PVD process. In the patent disclosure No. 57-65837, the piston ring is formed at least on the sliding surface with a coating of a titanium nitride, the coating having a hardness of greater than Hv 1300 and being 3 to 20 μm thick with a surface roughness less than 2 μm.

The piston ring proposed by these Japanese patent applications show better wear resistant property as compared with a piston ring having a hard chromium plating. It has however been noted that the coating as proposed by these Japanese patent applications has a poor adhesive property to the base metal and besides the thermal expansion coefficient of the coating material is significantly smaller than that of the base metal so that the coating is very easily peeled off the base metal during use in an internal combustion engine.

In order to improve the wear resistant property of the sliding surface of a piston ring, a nitrided layer may be provided in the sliding surface of the piston ring. This solution is not recommendable because the base metal which can be nitrided is relatively limited so that this measure cannot be widely adopted. Moreover, a nitrided layer is not as good in wear resistant property as the titanium nitride, titanium carbide or chromium nitride is.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a coating of a high wear resistance for a sliding surface which can be used even under a heavy thermal load condition.

Another object of the present invention is to provide a wear resistant coating for a sliding member which shows a strong resistance against peeling off the base material of the sliding member even under a sever thermal condition.

A further object of the present invention is to provide a method of producing such coating for a sliding surface.

According to the present invention, the above and other objects can be accomplished by a coating formed on a surface of a base material, said coating including a nitride of chromium, nitrogen concentration of said coating being increased from an interface between said base material and said coating continuously toward an outer surface of said coating. The coating may have an area adjacent to the outer surface which is essentially comprised of at least one of CrN and

Cr_2N.

According to the present invention, there is also provided a method of producing a coating on a sliding surface of a base material, the method comprising steps of providing the base material in a vapor deposition chamber, producing vapor of chromium in said chamber so that the chromium is deposited to form a coating on the sliding surface of said base material, introducing nitrogen into said chamber while the chromium is being deposited on said sliding surface of the base material so that a nitride of chromium is produced and deposited on said sliding surface of the base material forming at least a part of said coating, nitrogen concentration in said chamber being continuously increased so that nitrogen concentration in said coating is continuously increased from an interface between the base material and said coating toward an outer surface of the coating. In a preferable aspect of the present invention, the base material is heated while the coating is being formed, preferably to a temperature between 200 and 600 ^{o}C. The method may preferably be carried out under an evacuated non-oxidizing atmosphere and the nitrogen concentration may be changed continuously from 0 to 0.4 Pa ($3x10^{-3}$).

It has been found that the coating produced in accordance with the present invention has an outer surface having a wear resistance which is better than that of a hard nitrided chromium coating. The coating contains rich chromium in the vicinity of the base material so that it has a strong adhe-

sive power to the base material. It is therefore unlikely that the coating is peeled off the base material during use. The outer region of the coating contains mostly chromium nitride such as CrN, Cr_2N or a mixture of Cr and Cr_2N. Therefore, the coating shows an excellent wear resistance.

The temperature of the base material has an influence on the quality of the coating. It has been found that a temperature lower than 200 °C does not provide a coating having a significantly improved adhesive property to the base material. Under a temperature higher than 600 °C, the base material may be deformed and the surface hardness of the coating may be decreased. Where the nitrogen concentration is increased beyond 0.4 Pa ($3x10^{-3}$ torr), there may be a possibility that pores are produced in the coating causing a decrease in the surface hardness.

According the method of the present invention, deposition of chromium is started without introducing nitrogen into the chamber so that a layer of metal chromium is at first formed on the surface of the base material. The layer of chromium which may be referred as the base layer has a thermal expansion coefficient which is close to that of the base material. Therefore, there will be least possibility that the coating is peeled off the base material under a thermal effect. Thus, an improved adhesive power can be obtained. Further, the chromium rich layer adjacent to the base material has an excellent resiliency. This will further improve the anti-peel-off property of the coating.

The nitrogen concentration is gradually and continuously increased while the chromium is being deposited to form the coating on the sliding surface of the base material. A part of the vaporized chromium is then nitrided and deposited on the base material forming a part of the coating. The layer of the coating thus formed which may be referred as the second layer contains a mixture of chromium and chromium nitride and is of a greater hardness as compared with the base layer of chromium adjacent to the base material so that it possesses a higher wear resistant property than the base layer. Further, the second layer has a sufficient resiliency so that the adhesive property of the base layer will not be adversely affected by the second layer.

The coating in accordance with the present invention can be used in any type of sliding member such as a piston ring and an oil ring of an internal combustion engine and a rail on which a rolling or sliding member is moved.

The above and other objects and features of the present invention will become apparent from the following description of a preferred embodiment and examples taking reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic illustration of an ion plating apparatus for producing the coating in accordance with the present invention;

Figure 2 is a diagram showing the results of X-ray analysis of the coating formed in accordance with the present

invention; and,

Figure 3 is a diagram showing effects of nitrogen concentration on wear resistant property of the coating.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to the drawings, particularly to Figure 1, there is shown an ion plating apparatus which can be used for the present invention. The apparatus includes a housing 9 in which a crucible 6 is located. The crucible 6 is adapted for receiving a metal 5 to be vaporized for vapor deposition. In accordance with the present invention, the metal 5 is chromium. An electron gun 8 is provided above the crucible 6 for applying electron beam to the metal 5 in the crucible 6 so that the metal 5 is vaporized. Around the crucible 6, there is provided a condensing coil 7 for focusing the electron beam from the electron gun 8 to the metal 5 in the crucible 6.

Above the crucible 6 and the electron gun 8, there is provided a base metal support 2 for supporting a base metal 1 on which a coating of chromium is to be produced. A shutter 10 is retractably provided between the crucible 6 and the support 2. A nitrogen supply tube 11 is provided to supply nitrogen into the chamber in the housing 9. A heating device 3 is provided above the base metal support 2 for heating the base metal 1 on the support 2.

As an example, a corrosion resistant steel meeting the Japanese Industrial Standard (JIS) SUS-440C may be used as the base metal 1. The base metal is cut into a piece of 50

mm wide, 50 mm long and 10 mm thick and placed on the base metal support 2. The chamber in the housing 9 is then evacuated and argon gas is introduced into the chamber through the tube 11 to a pressure of 13 Pa ($1x10^{-1}$ torr). In order to clean the surface of the base metal 1, electric voltage is applied between the base metal 1 and the housing 9 to produce an electric discharge with the base metal 1 as a cathode.

The base metal 1 is then heated to a temperature of 400°C and the chamber in the housing 9 is evacuated to a pressure of 6.7 mPa ($5x10^{-5}$ torr). The electron beam is then applied by the electron gun 8 to the chromium 5 in the crucible 6 to make the chromium vaporized. The shutter 10 is retracted so that the vaporized chromium is deposited on the base metal 1. After 30 seconds, nitrogen gas is started to be introduced into the chamber in the housing 9 through the tube 11. The supply of the nitrogen gas is increased continuously so that the nitrogen concentration reaches 0.4 Pa ($3x10^{-3}$ torr) in terms of the partial pressure of nitrogen gas in 20 minutes. The partial pressure of the nitrogen gas is maintained for a time period of 2 minutes and the shutter 10 is inserted to the position shown in Figure 1 to terminate the vapor deposition process. The base metal 1 is cooled and taken out of the housing 9. The electron gun 8 is energized with an electricity of 35 volts, 500 amperes and the condensing coil 7 is energized with a current of 250 amperes. The maximum flow of the nitrogen gas is 1000 cm^3/min.

Various tests have been made with specimens prepared in

accordance with the process described above. The results will follow.

(1) Analysis of nitrogen and chromium concentrations by means of an X-ray micro-analyzer

In order to determine a change in concentrations of chromium and nitrogen in the coating, the specimen was cut and the section was subjected to an X-ray analysis by means of an X-ray analyzer. The results are shown in Figure 2. In Figure 2, it will be noted that the chromium concentration shows the maximum value in the portion of the coating adjacent to the base metal and gradually decreases toward the outer surface. The nitrogen concentration shows the minimum value in the portion of the coating adjacent to the base metal and gradually increases toward the outer surface.

(2) X-ray refraction analysis of the composition in the vicinity of the outer surface of the coating

An X-ray analysis was made in order to determine the composition of the outermost part of the coating. It has been confirmed that the outermost part of the coating is made of CrN, Cr_2N or a mixture of them.

(3) Shock resistant test

A shot-blast test was conducted to determine the anti-peel-off property of the coating. Steel balls of 1 to 2 mm diameter were blasted against the coating and the time was measured until the coating was peeled off the base metal.

Comparative test specimens were prepared for this and subsequent tests by forming coatings on base metals through

ion plating process in which the nitrogen partial pressure was maintained at a constant value of 0.4 Pa ($3x10^{-3}$torr) throughout the process. The comparative test specimen was subjected to the same shot blast test.

It has been confirmed that the coating on the comparative test specimen showed a partial peel off after 10 minutes of the start of the shot blasting. In 15 minutes, substantially all of the coating was peeled off the base metal. To the contrary, the coating in accordance with the present invention showed a remarkably improved anti-peel-off property against shot blasting.

(4) Thermal fatigue

In order to determine the durability against repeated cycles of heating and cooling, the specimens were subjected to repeated cycles of heating from the room temperature to 450°C, maintaining the specimen under the temperature for 1 minute , cooling to the room temperature in 1 minute , maintaining the specimen under the room temperature for 1 minute and heating again. It has been found that in the comparative test specimen crack has been produced after 250 cycles of the heating and cooling and a partial peel-off was observed after 500 cycles. The specimen in accordance with the present invention has shown no defects even after 500 cycles. It has thus been confirmed that the coating made in accordance with the present invention has a remarkably improved resistance to thermal fatigue.

(5) X-ray refraction analysis

It is understood that the coating made in accordance with the present invention has a chemical composition which continuously changes with depth from the inner part adjacent to the base metal to the outer surface. It is however very difficult to verify this fact through an X-ray refraction test. Therefore, in order to simulate the coating, a plurality of coatings were prepared under constant but different values of nitrogen partial pressure. The coatings thus prepared were subjected to X-ray refraction analysis. The results are shown in the table.

In the table, it will be understood that the coating in accordance with the present invention will undoubtedly have nitrogen concentration which gradually increases from the inner part adjacent to the base metal toward the outer surface.

Table

specimen	nitrogen partial pressure	coating
A	0.04 Pa($0.3x10^{-3}$ torr)	Cr, Cr_2N
B	0.09 Pa($0.7x10^{-3}$ torr)	Cr, Cr_2N
C	0.13 Pa($1.0x10^{-3}$ torr)	Cr_2N
D	0.20 Pa($1.5x10^{-3}$ torr)	Cr_2N, CrN
E	0.40 Pa($3.0x10^{-3}$ torr)	CrN

It should be noted that the coating in accordance with the present invention contains rich chromium in the portion close to the base metal. It is understood that this feature contributes to the improvement of the properties under the shock resistant and thermal fatigue tests.

(6) Wear test

The specimen having a coating in accordance with the present invention was subjected to a wear test. For the purpose, the specimen was prepared in the form of a pin which was brought into contact with a drum made of Japanese Industrial Standard (JIS) FC-25 steel. The specimen was forced against the drum under a load of 2 kg and the drum was rotated with a linear speed of 0.25 m/sec. A pH 2 water solution of sulfuric acid was used as a lubricant. As a comparative specimen, a pin having a hard chromium plating was prepared and subjected to the same test. The results are shown in Figure 3.

It will be noted in Figure 3 that the coating in accordance with the present invention shows a remarkably improved wear resistant property as compared with a hard chromium plating. The results shown in Figure 3 shows that the coating in accordance with the present invention has the highest wear resistance in the part where the coating was produced under the nitrogen partial presure 0.13 to 0.20 Pa (1.0 to 1.5×10^{-3} torr). Under this condition, the coating contains mostly Cr_2N or Cr_2N+CrN. It will therefore be understood that the nitrogen partial pressure should preferably maintained in the final stage of the ion plating process to a value of 0.13 to 0.20 Pa (1.0 to 1.5×10^{-3}torr).

CLAIMS:

1. A wear resistant coating provided on a base material, said coating including a nitride of chromium, wherein the nitrogen concentration of said coating continuously increases from the interface between said base material and said coating towards the outer surface of said coating.

2. A wear resistant coating in accordance with claim 1 in which said coating has a layer adjacent to said base material which consists substantially of chromium.

3. A wear resistant coating in accordance with claim 1 or claim 3 in which said coating has a layer adjacent to the outer surface which consists substantially of at least one of CrN, Cr_2N and a mixture of Cr_2N and CrN.

4. A sliding member including a base metal and, formed on at least one sliding surface of said base metal, a coating in accordance with any preceding claim.

5. A sliding member in accordance with claim 4 in which said base metal is a piston ring of an internal combustion engine.

6. A method of producing a coating on a surface of a base material, the method comprising the steps of positioning the base material in a vapor deposition chamber; producing chromium vapor in said chamber so that the chromium is deposited to form a coating on the surface of said base material; introducing nitrogen into said chamber while the chromium is being deposited so that a nitride of chromium is produced and deposited on said surface of the base material forming at least a part of said coating, the nitrogen concentration in

said chamber being continuously increased so that the nitrogen concentration in said coating continuously increases from the interface between the base material and said coating towards the outer surface of the coating.

7. A method in accordance with claim 6, in which the base material is heated while the coating is being formed.

8. A method in accordance with claim 7, in which said base material is heated to a temperature between 200 and 600°C.

9. A method in accordance with any of claims 6 to 8, which is carried out under an evacuated non-oxidzing atmosphere and in which the nitrogen concentration is increased continuously from 0 to a maximum of 0.4 Pa ($3x10^{-3}$ torr).

10. A method in accordance with any of claims 6 to 8, which is carried out under an evacuated non-oxidizing atmosphere and in which the nitrogen concentration is increased continuously from 0 to a maximum of 0.2 Pa ($1.5x10^{-3}$ torr).

11. A method substantially as described herein with reference to Figure 1.

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